STRUCTURAL AND MECHANICAL EFFECTS
OF INTERSTITIAL SINKS

by

Mark J. Klein

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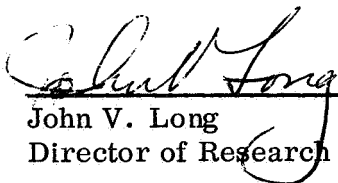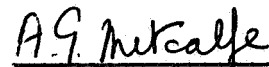Headquarters, Washington, D. C. 20546

ABSTRACT

The contribution of solutes to the creep strength of columbium and tantalum base alloys is being studied through their effect on the activation energy for creep. In this regard, a comparison of creep data for columbium and D43 suggests that the solid solution strengtheners contribute much more to the creep strength of D43 near $0.5\,T_M$ than does the carbide dispersion. The activation energy and the stress dependence of the creep rate for D43 were determined over a range of temperatures and stresses. The activation energy, H, between 1600 and 3300°F is given by the equation $H = 0.034\,(2300 - T) + 110$ where T is the temperature in °F and H is in K cal/mole. The stress dependence of the creep rate $(\overset{\circ}{\epsilon})$ over this temperature range can be expressed by the proportionality, $\overset{\circ}{\epsilon} \alpha\ e^{B\sigma}$ where B is a constant and σ is the stress.

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INTRODUCTION

This is the sixth quarterly progress report for the Contract NAS-7-469, "Structural Effects of Interstitial Sinks" covering the period March 8, 1968 through June 8, 1968.

In many practical applications it is necessary to use a refractory metal in contact with a more reactive metal. Under these conditions, the interstitial elements in the refractory metal tend to concentrate in the more reactive metal (interstitial sink). This partition of interstitials can cause a serious decrease in the elevated temperature strength of the refractory metal. The first part of this program was primarily concerned with the change in structure, strength, and interstitial concentration in a refractory alloy induced by an interstitial sink. During the preceding period the loss of carbon from D43 (a columbium base alloy strengthened with a carbide dispersion) to a titanium sink was correlated with the creep behavior of the D43. The creep rate of D43 near $0.5 T_M$ was found to be proportional to the carbon lost to the interstitial sink.

During the period covered by this report the scope of the program was broadened to include the effect of substitutional solutes on the creep rate of columbium and tantalum base alloys. Since creep is thermally activated, the creep rate is a sensitive function of the magnitude of the activation energy for creep. Therefore, the influence of solutes on creep is being studied through their effect on the activation energy for creep. This part of the program was initiated with a study of the effect of solutes on the activation energy for creep of D43. Other alloys will be selected to sort out the effect of the various solute constituents on the creep rate of columbium and tantalum base alloys. This phase of the investigation should provide information concerning the role that various solute additions play in strengthening refractory alloys.

The experimental procedures used in this investigation have been reported in the interim report covering the period 8 June, 1966 through 8 June, 1967. Therefore, experimental procedures will be considered in this report only when new techniques are involved.

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RESULTS AND DISCUSSION

Data are presented in this section showing the temperature and stress dependence of the strain rate for D43 over a range of temperatures and stresses. This information will provide a basis to compare the creep behavior of D43 with that of other columbium base alloys to be tested in subsequent work. These tests are designed to reveal the contribution of various solutes to creep strength. Here, creep strength is used in a qualitative way to designate the resistance to high temperature deformation, i.e., the stress at constant strain rate and temperature or the strain rate at constant stress and temperature. The principle parameter to be used to sort out the effect of various solutes on the creep strength is the activation energy for creep. This parameter is a sensitive measure of both the creep rate and the high temperature deformation mechanism. Its measurement, therefore, should provide information about the contribution of solutes to creep strength and their effect on the deformation mechanisms. An additional factor important in determining the creep strength is the stress sensitivity of the creep rate. Therefore, this factor will also be considered as needed to determine the effect of solute additions on creep behavior.

2.1 CREEP OF D43

During the period covered by the interim report for the period 8 June, 1967 to 8 March, 1968, it was found that the creep rate, $\overset{\circ}{\epsilon}$, of D43 at 2200° F could be expressed by the equation

$$\overset{\circ}{\epsilon} = A \sigma^n \exp -H/RT \tag{1}$$

where A is a function of the carbon concentrations, σ is the stress, n is the stress exponent, and H is the activation energy for creep. The values of n and H were found to depend somewhat upon the processing condition of the as-received alloy. For D43 processed by Fansteel in the duplex condition (Dup F), H was about 110 K cal/mole above 2300°F, a value approximately equal to the activation energy for self-diffusion. At lower temperatures preliminary measurements indicated that the activation energy for creep was greater than that for self-diffusion. However, excessive scatter in activation energy measurements at low temperatures made it difficult to establish this point. In addition, within the range of stress variations tested at 2200°F it was not possible to distinguish between the proportionalities, $\overset{\circ}{\epsilon} \alpha \sigma^n$ and $\overset{\circ}{\epsilon} \alpha e^{B\sigma}$, although the latter expresses a much stronger dependency of the strain rate on the stress than the former. Thus, at the conclusion of the previous period the

activation energy below $0.5 T_M$ ($\sim 2300°F$) was not well defined, and the stress dependence of the strain rate was not unambiguously established. However, it is important to know the stress and temperature dependence of the creep rate if the factors contributing to the creep strength of D43 are to be sorted out.

During this period, the activation energy for creep of D43 was determined in the range 1600-2300°F, and the proportionality between the creep rate and the stress was more clearly defined.

2.1.1 Stress and Temperature Dependence of the Creep Rate

It has been shown that high temperature creep data can often be correlated by an equation of the form (Ref. 1)

$$\overset{\circ}{\epsilon} = f(\sigma, S) e^{-H/RT} \tag{2}$$

where $\overset{\circ}{\epsilon}$ is the steady state creep rate, σ is the stress, S is a structure factor. In this equation H is independent of stress and temperature and is usually equal to the activation energy for self-diffusion. Eq. 2 can be written

$$\overset{\circ}{\epsilon} e^{H/RT} = f'(S) \text{ for } \sigma = \text{constant} \tag{3}$$

and where $\ln \overset{\circ}{\epsilon}$ is linear with $1/T$, H and f'(S) are constant.

If S is a function of only the creep stress,

$$\overset{\circ}{\epsilon} e^{H/RT} = F(\sigma), \tag{4}$$

and a linear plot of Eq. 4 will reveal $F(\sigma)$. A trade off between temperature and stress can be used to maintain the strain rate at a convenient rate while investigating the effect of large variations in stress. For example, the term $\overset{\circ}{\epsilon} \exp H/RT$ (a temperature compensated strain rate) when plotted against $F(\sigma)$ may be useful in distinguishing between exponential and power stress dependencies in Eq. 2. However, $F(\sigma)$ in Eq. 4 includes both a stress and structure dependency and, therefore, its determination will not unambiguously reveal the stress dependency of the strain rate.

The creep data between $\sim 2200°F$ and $\sim 3300°F$ are shown in Figures 1 and 2 for a logarithmic plot of Eq. 4 where $F(\sigma) = Ae^B$ and $F(\sigma) = A'\sigma^n$ with $H = 110K$ cal/mole (see Interim Report 8 June, 1967 - 8 March, 1968). The number in parentheses near the datum points indicates the number of experimental measurements for a particular stress. The higher stress measurements were made at lower temperatures and the lower stress measurements were made at higher temperatures. It is evident that the creep data between 2200°F and 2300°F can be correlated better with
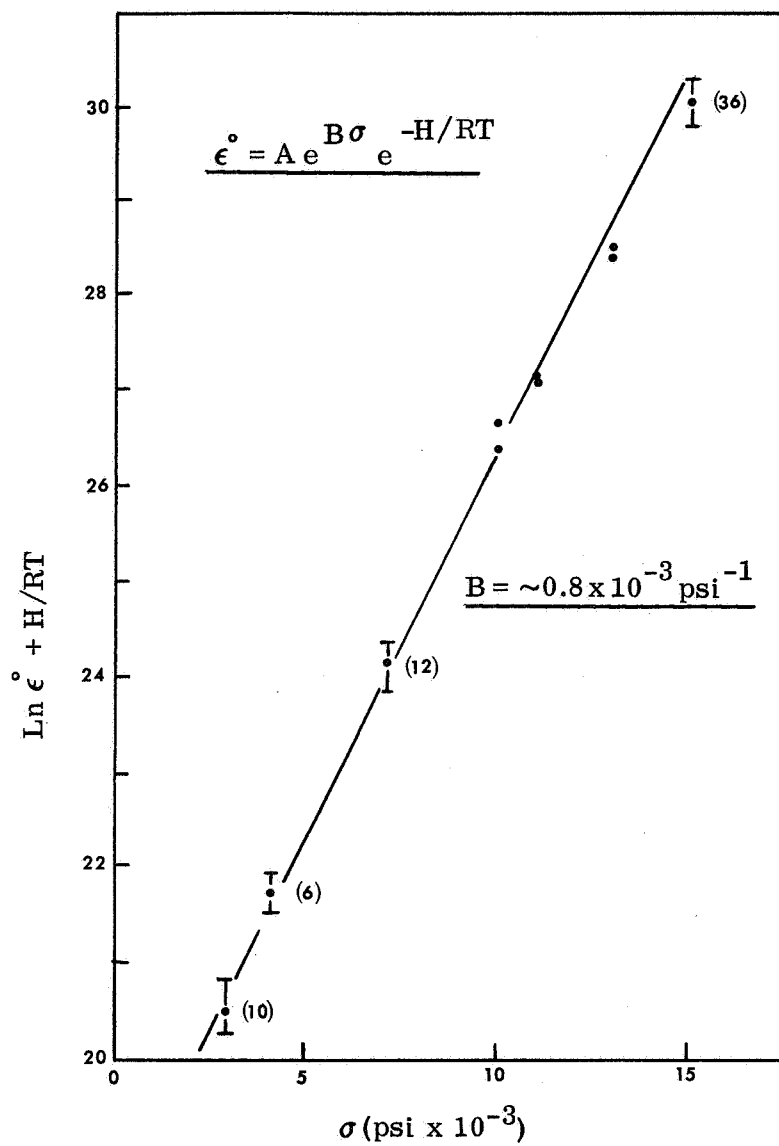
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FIGURE 1. TEMPERATURE-COMPENSATED CREEP RATE AS A FUNCTION OF THE APPLIED STRESS $(T > 0.5\,T_M)$
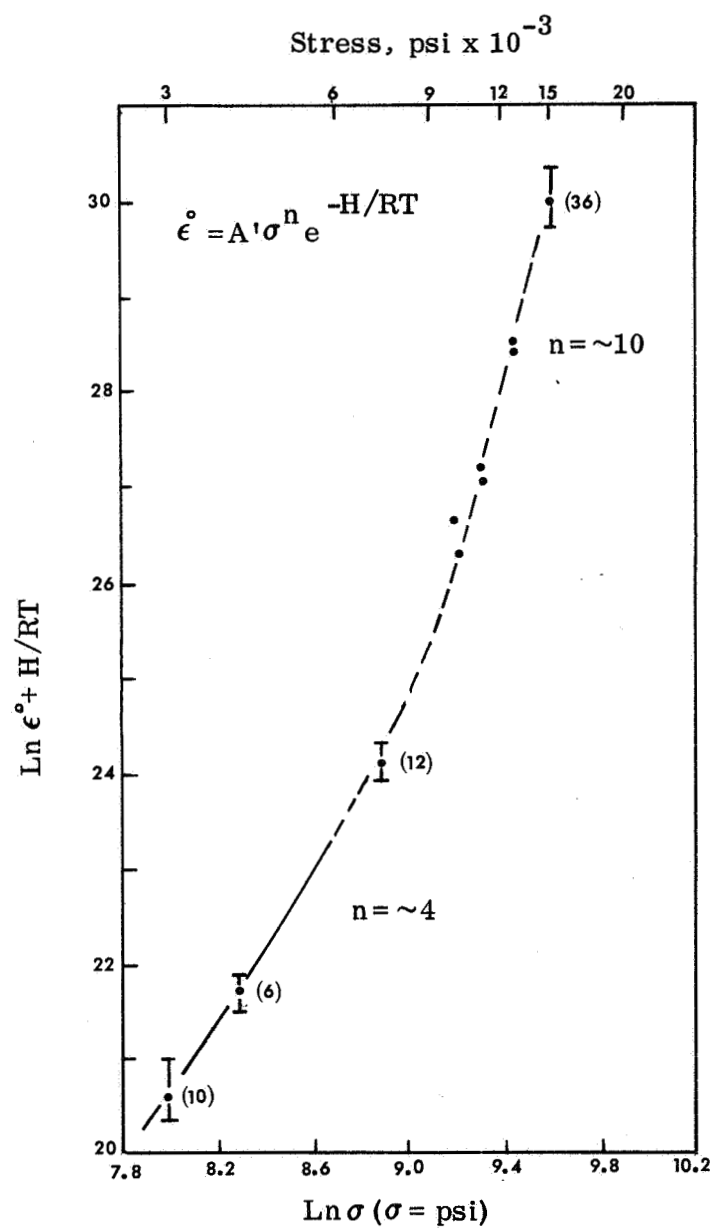
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FIGURE 2. TEMPERATURE-COMPENSATED CREEP RATE AS A FUNCTION OF THE LOGARITHM OF APPLIED STRESS (T $>0.5\,T_M$)

an exponential stress dependency than with a power stress dependency. Therefore, in this temperature range

$$\overset{\circ}{\epsilon} e^{H/RT} = F(\sigma) = A e^{B\sigma} \tag{5}$$

where H and A are constants.

The experimental data over the entire range of temperature and stress tested are shown in Figure 3 (solid line) for the exponential stress dependency were $H = 110K$ cal/mole over the entire range of stress. In these tests the temperature and stress vary from 3 ksi in the temperature range 3000-3300 F to 44 ksi in the temperature range 1600-1700°F. Although the data in the high temperature low stress region correlate reasonably well for $F(\sigma) = A e^{B\sigma}$, the data in the low temperature, high stress region do not obey this function, if H is assumed to be constant and equal to 110 K cal/mole.

Without regard to the mechanisms involved, there are a number of reasons that may account for the failure of Eq. 4 below about $0.5 T_M$. For example, B may vary or the $F(\sigma)$ function used in Eq. 5 may not be the correct one in the low temperature high stress range.   Eq. 4 is based upon the assumption that the structure is a function of only the stress. However, it may also be a function of the temperature or perhaps the strain. These possibilities can be at least partly checked by determine $F(\sigma)$ for a series of isothermal tests to see if the stress function is different at different temperatures and stresses.

The dependence of strain rate on stress at 2800°F, 2200°F, and 1750°F is shown in Figures 4 and 5 for $\overset{\circ}{\epsilon} a e^{B\sigma}$ and $\overset{\circ}{\epsilon} a \sigma^n$. The exponential relationship (Fig. 4) is approximately linear for all of these temperatures, whereas the power relationship (Fig. 5) is nonlinear at 2800°F. In addition, B is approximately constant at the three temperatures while   n   varies from 3.5 to 30.   Therefore, the $e^{B\sigma}$ term in Eq. 5 is probably a reasonable function to use in correlating stress variations over the range of temperatures tested. In this regard, it was shown in the previous report that if B is constant, n must vary with stress according to the relationship

$$n = \sigma B \tag{6}$$

The data of Figures 4 and 5 obey this equation very well.

Another reason why Eq. 5 does not apply in the high-stress low-temperature region (Fig. 3) may be that H is a function of stress, temperature, structure or combinations of these variables and, therefore, is not constant. This possibility can be investigated by determining H over the range of stress and temperature variations used in these tests. The results shown in Figure 6 suggest that H is a variable below 2300°F since it increases from about 110 K cal/mole at this temperature to about 130 K cal/mole at 1700°F. Therefore, the failure of Eq. 5 below $\sim 0.5 T_M$ may be caused by the

$\dot{\epsilon}^\circ = A\,e^{B\sigma}\,e^{-H/RT}$

Low Temp.
High Stress
Region

$B = 0.78 \times 10^{-3}\,\text{psi}^{-1}$

High Temp.
Low Stress
Region

Ln $\dot{\epsilon}^\circ$ + H/RT

• ——— Data Plotted For H = 110,000 cal/mole

✕ — — — Data Plotted For H Given by Eq. 7
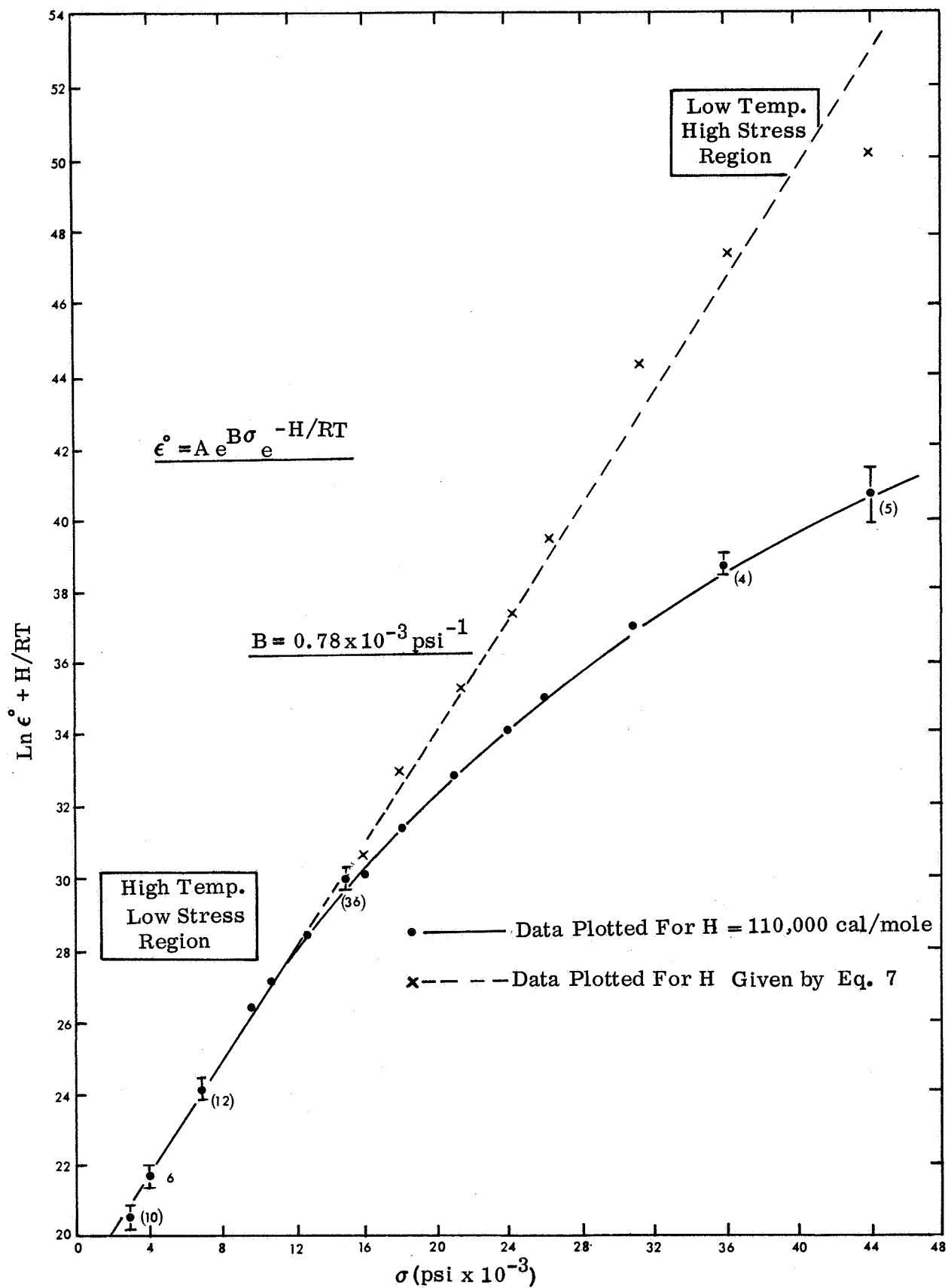
$\sigma\,(\text{psi} \times 10^{-3})$

FIGURE 3. THE TEMPERATURE-COMPENSATED CREEP RATE AS A FUNCTION
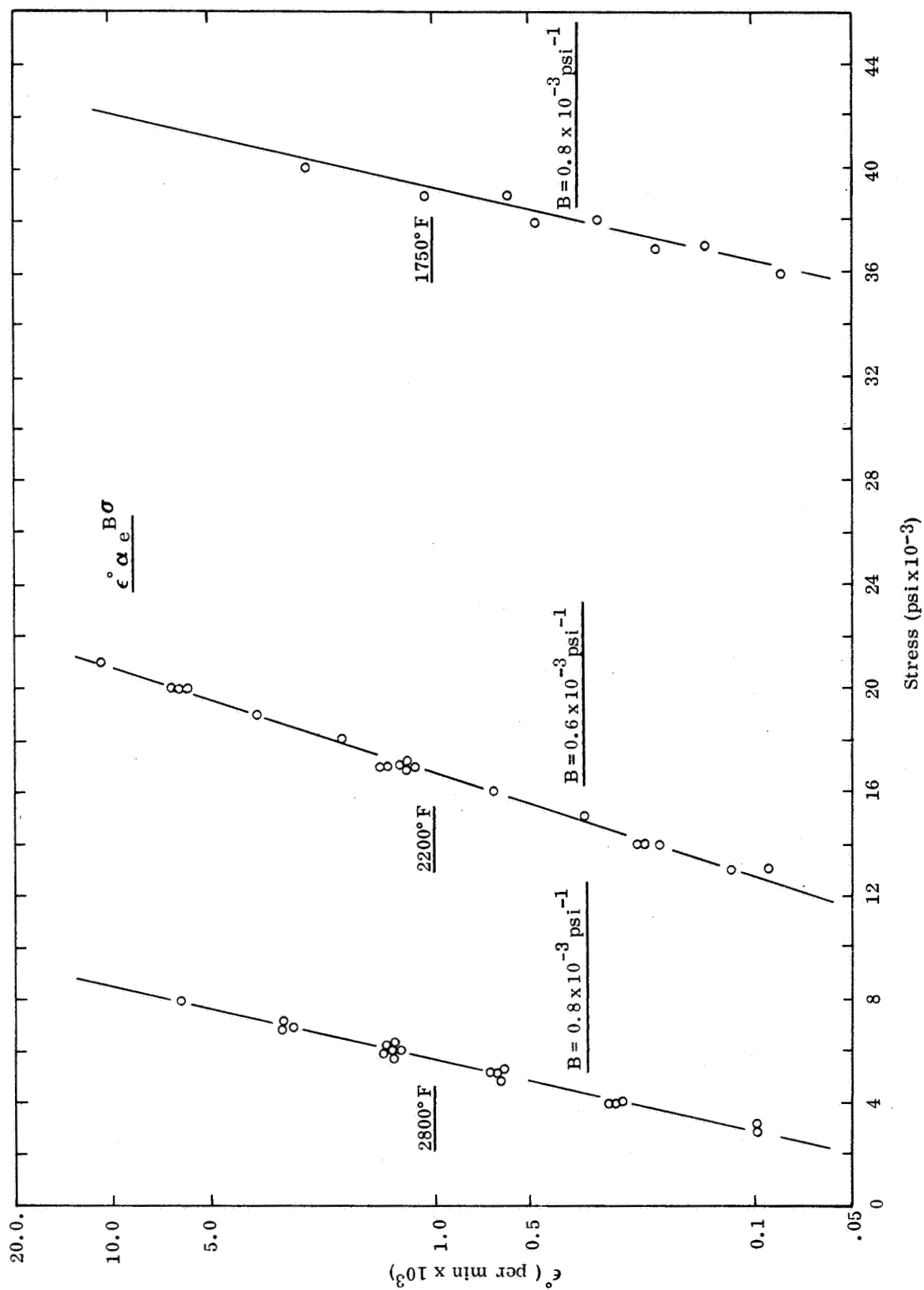OF THE APPLIED STRESS

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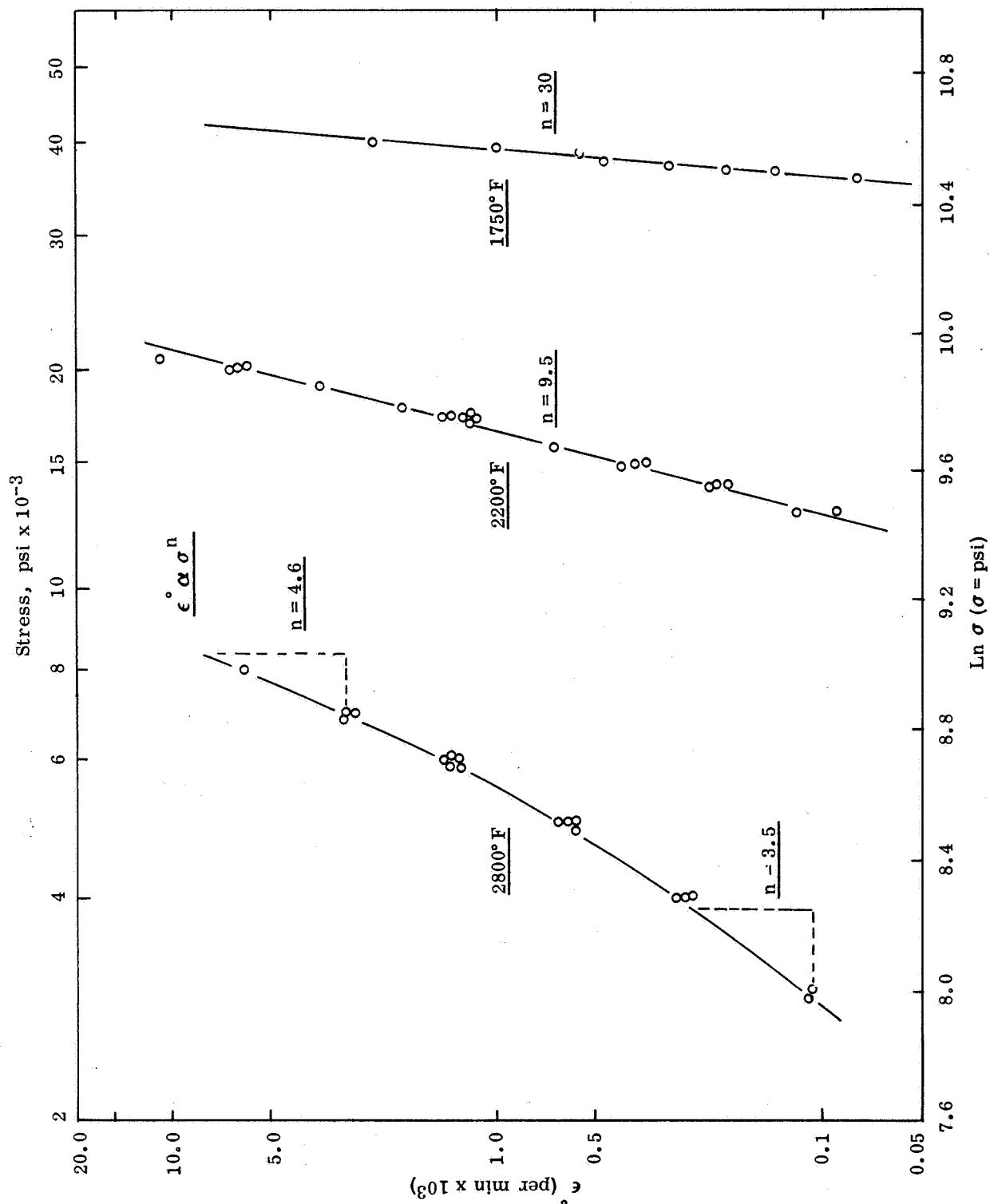FIGURE 4. THE STRESS DEPENDENCE OF THE CREEP RATE FOR $\dot{\epsilon}^{\circ}\,\alpha\,e^{B\sigma}$

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FIGURE 5.   THE STRESS DEPENDENCE OF THE CREEP RATE FOR $\dot{\epsilon}^o \alpha \sigma^n$

increase in H at lower temperatures. The approximate range for self-diffusion in D43 is indicated in the center of Figure 6. The variables responsible for the increase in activation energy to values above that for self-diffusion are difficult to ascertain because the higher values were obtained at lower temperatures, greater stresses and with different internal structures. However, the data can be empirically correlated using activation energy values determined from the dashed line in Figure 6 between 1600 and 2300°F. As shown in Figure 3 (dashed line) the data will yield an approximate linear relationship over the entire range of stress and temperature tested if a variable activation energy derived from the experimental data is used below $\sim 0.5\,T_M$. The slope of the line in Figure 3 yields $B = 0.78 \times 10^{-3}\,psi^{-1}$ in good agreement with the values of B determined from the isothermal data shown in Figure 4. Therefore, Eq. 5 will describe the creep of D43 over the entire range of temperature and stress tested when $A = 1 \times 10^8$, $B = 0.78 \times 10^{-3}\,psi^{-1}$ and H has the values determined experimentally. H is 110 K cal/mole above 2300°F but below this temperature the approximate value of H is given by the linear equation,

$$H = 0.034\,(2300\text{-}T) + 110. \tag{7}$$

In Eq. 7, T is the temperature in °F and H is in K cal/mole. This is only an approximate relationship since the low temperature activation energies are probably a much more complex function involving stress, temperature and structure.

In summation, the creep rate of D43 can be expressed by the equation

$$\epsilon^\circ = A e^{B\sigma} e^{-H/RT} \tag{8}$$

where B is 0.6 to $0.8 \times 10^{-3}\,psi^{-1}$ and A is constant. H is 110 K cal/mole between 2300 and 3300°F but between 2300°F and 1600°F, H increases with decreasing temperature according to Eq. 7.

The isothermal variation of strain rate over a small range of stress variation can be expressed by either of the proportionalities $\epsilon^\circ \alpha \sigma^n$ or $\epsilon^\circ \alpha\, e^{B\sigma}$. However, since B is approximately constant ($\sim 0.8 \times 10^{-3}\,psi^{-1}$), n must vary with stress according to the equation $n = \sigma B$. The variation of n with stress was shown in a series of isothermal tests at different temperatures (Fig. 5).

2.1.2 Dispersion and Solute Contributions to the Creep Strength of D43 at 2200°F

D43 is a columbium-base alloy strengthened by a dispersion (a complex carbide) and by the solid solution strengtheners, tungsten and zirconium (in excess of that required to form the carbide dispersion). In this section an estimate is made of the relative contributions of the carbide dispersion and the solid solution strengtheners to the creep strength and the strain rate of D43. The estimate is based upon comparisons
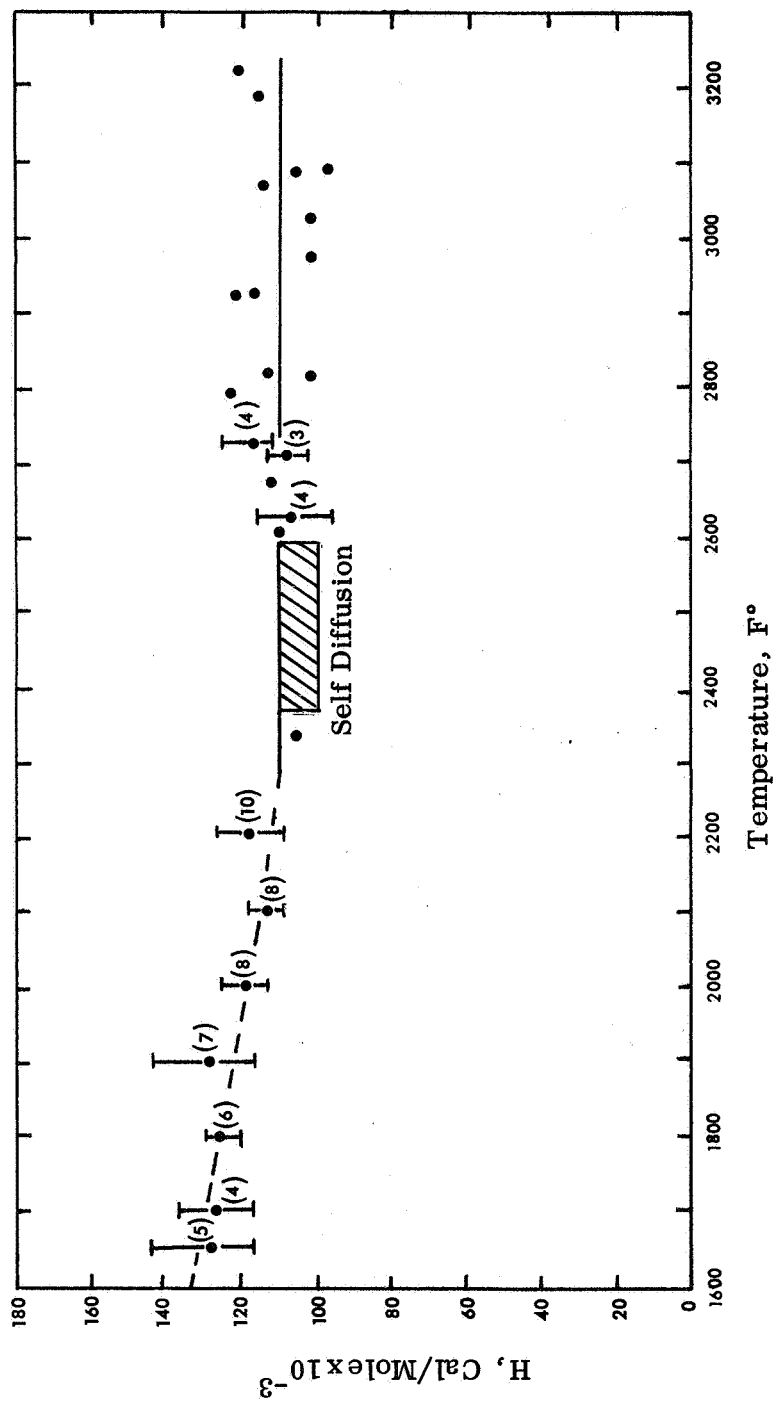
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FIGURE 6. THE ACTIVATION ENERGY FOR CREEP OF D43 OVER A RANGE OF TEMPERATURES

of the stresses and strain rates at 2200° F for the following: D43 before it is subjected to an interstitial sink (dispersion and solution strengthened), D43 after it is subjected to an interstitial sink (solution strengthened), and columbium (neither solution nor dispersion strengthened).

In past work it was shown that the carbon concentration and, therefore, the amount of carbides in D43 can be drastically reduced by the action of a titanium interstitial sink. This is illustrated in Figure 7 where the structures of D43 are shown after the alloy is annealed with and without a titanium sink. After the alloy is subjected to the sink, the carbide dispersion which is evident in the as-processed and as-annealed conditions can no longer be detected. Therefore, a comparison of the creep rates and stresses at the same temperature before and after the sink treatment will reveal the contribution of the carbides to the creep strength of D43. As shown in Table I, for a stress of 15 ksi, the steady state creep rate at 2200° F for sink treated D43 (annealed 57 hours at 2200° F with Ti) is about twenty times greater than that of D43 similarly heat treated without a sink. This increase in creep rate induced by the sink can be primarily attributed to the loss of the dispersion since previous work (Interim Report 8 June, 1967 - 8 March, 1968) has shown that the subgrain and dislocation networks do not play an important role in strengthening this alloy near $0.5 T_M$. Therefore, the loss of the carbide dispersion increases the creep rate of D43 by a factor of about twenty.

The contribution of the solid solution strengtheners to the creep rate of D43 can be estimated by comparing the creep rate of sink-treated D43 (dispersion removed) with that of unalloyed columbium. The creep tests for D43 and Cb were performed at the same temperature (2200° F) but because of the great difference in strength, it was necessary to test the columbium at a much lower stress than the D43. Therefore,

TABLE I

A COMPARISON OF CREEP BEHAVIOR AT CONSTANT STRESS (σ) AND CONSTANT STRAIN RATE (ϵ°)

EXPERIMENTAL DATA			COMPARISON AT —			
			Constant Stress		Constant Strain Rate	
Specimen	ϵ° %/min x 10^2	σ ksi	ϵ° %/min x 10^2	σ ksi	ϵ° %/min x 10^2	σ ksi
D43 (Annealed without sink)	1	15	1	15	1	15
D43 (Annealed with sink)	20	15	20	15	1	10.5
Cb (Recrystallized)	1	2	24,000	15	1	2
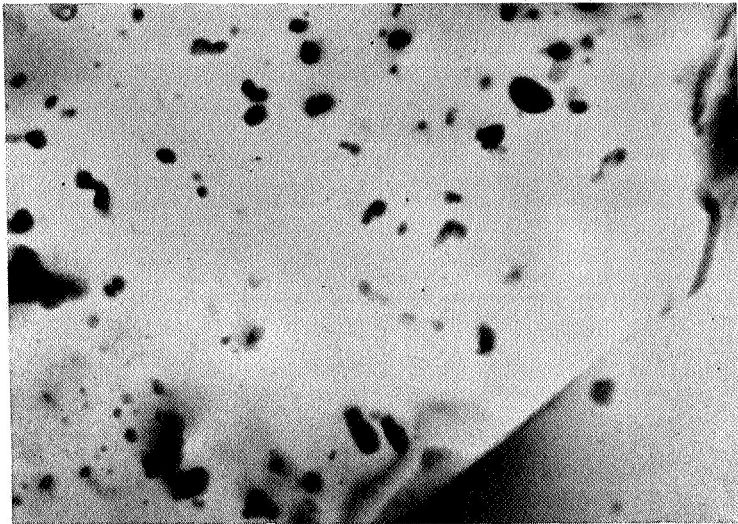
Annealed Without a
Titanium Sink
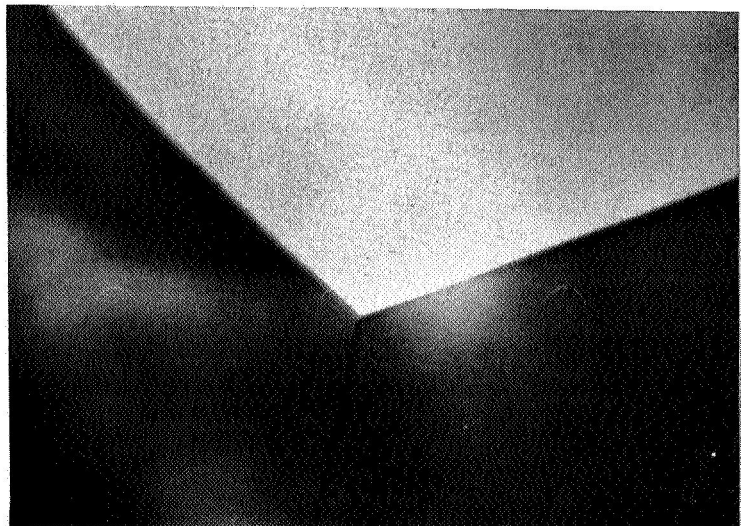
Annealed With
a Titanium Sink

FIGURE 7. THE REDUCTION IN THE CARBIDE DISPERSION INDUCED BY A
TITANIUM INTERSTITIAL SINK

the D43 was tested using a stress of 15 ksi and the Cb was tested with a stress of 2 ksi. An adjustment was made for this stress differential by using the published proportionality between strain rate and stress for columbium, i.e., $\overset{\circ}{\epsilon} \alpha \sigma^5$, (Ref. 2). As shown in Table I, the strain rate of columbium would be 24,000%/min if it were tested at the same stress as D43 (i.e., 15 ksi). This is, of course, only a rough approximation to indicate the order of magnitude of the columbium strain rate on an equal stress basis.

Thus, if we construct D43 by first adding the solid solution strengtheners, W and Zr to Cb, the creep rate is reduced by a factor of about 24,000 to 20 or 1200/1. The subsequent addition of the carbide dispersion (formation of complex carbides) induces an additional reduction in the creep rate of about 20 to 1. On this basis, the soluble additions to D43 play a dominant role in strengthening this alloy at this temperature.

By using a similar procedure, the stress required for equal strain rates at 2200°F can be compared for D43, D43 (sink treated) and Cb. Here, the proportionality between strain rate and stress determined previously in this investigation (i.e., $\overset{\circ}{\epsilon} \alpha \sigma^8$) was used to compare the stress at equal strain rates. As shown in the last two columns in Table I, the stresses required for equal strain rates for D43, D43 (sink treated) and Cb are in the proportions 15 to 10.5 to 2 or 7.5 to 5.3 to 1 respectively. Therefore, although the carbide dispersion contributes to the creep strength of D43, the primary strength of this alloy at 2200°F is derived from solid solution strengthening. At higher temperatures where the dispersed phase is less stable, the relative contribution of the solute constituents will tend to increase. Thus, it is important to determine the way that the solutes can influence creep strength.

One way that solutes can increase the creep strength of alloys is by increasing, H, the activation energy for creep. In this regard, the activation energy for creep is often equal to that for self-diffusion. Therefore, if solute additions increase the melting point of the alloy, they also tend to increase the activation energy for self-diffusion and creep. This tends to strengthen the alloy at high temperatures. Once the alloy metal has been selected for melting point (and thus activation energy for creep), the high temperature creep performance can be improved further by control of substructure, incorporation of disperse phases and other methods that affect primarily the terms other than the Boltzmann term in Equations 1 and 8. However, it is important to appreciate that the creep rate at elevated temperatures is generally limited by the maximum value that the activation energy for creep can attain which is that for self-diffusion in the alloy.

A way in which H can be increased above that for self-diffusion is to develop an alloy in which a solute-dislocation interaction creates a stable dislocation atmosphere. Here, the activation energy for creep becomes that required to move the entire atmosphere rather than that for a vacancy-atom interchange characteristic of dislocation climb. Under the conditions where the drift velocity of the atmosphere is approximately

equal to the dislocation velocity the effective activation energy may exceed that for self-diffusion. Examples of this behavior are Zircaloy (Ref. 3), nickel (Ref. 4) and Al-3.2Mg (Ref. 5). The activation energy for creep in a certain temperature range for each metal is above the activation energy for self-diffusion. Another instance of this behavior may be the increase in H shown in Figure 6 for D43 below about 2300°F. Here, H increases from about 110K cal/mole above 2300°F to about 130 K cal/mole at 1600°F. This relatively small increase in H will have a marked effect on the creep rate. For example, the creep rate will decrease by a factor of 4000 at 1700°F if H increases from 110 to 130 K cal/mole.

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SUMMARY AND CONCLUSIONS

The influence of solutes on the creep strength of columbium and tantalum base alloys is being studied through their effect on the activation energy for creep. During this period the activation energy and the stress dependence of the creep rate were determined for D43 over a range of temperatures and stresses. This information will provide a basis for comparison of the creep behavior of other columbium base alloys selected to sort out the effect of solutes on creep behavior.

The creep rate of D43 between 1600 and 3300°F can be expressed empirically by the equation

$$\overset{\circ}{\epsilon} \simeq A e^{B\sigma} e^{-H/RT}$$

where B and A are constants. Above 2300°F, H is 110 K cal/mole, but below this temperature H varies according to the equation

$$H = 0.034 \, (2300-T) + 110$$

where H is in K cal/mole and T is the temperature in °F. The increase in H below 2300°F to values above the activation energy for self-diffusion is anomolous since in this temperature region ($< 0.5 \, T_M$) H is expected to decrease in analogy with the behavior of fcc metals. This increase in H could reflect a significant increase in the creep strength of this alloy since the creep rate (and thus the strength) is a sensitive function of H.

The effect of various solutes on the activation energy for creep will be investigated further in subsequent work by testing columbium base alloys of varying composition. In this regard, a comparison of creep data for columbium and D43 at 2200°F suggests that the solutes contribute much more to the creep strength of D43 than does the carbide dispersion.

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FUTURE WORK

The creep behavior of a number of columbium and tantalum base alloys will be studied to determine the contribution of solutes to the elevated temperature strength of these alloys. The alloys will be selected to sort out the influence of various solutes on the creep strength through their effect on the activation energy for creep. This study should provide information of the value in selecting solutes to optimize the high temperature strength of alloys.

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